PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

MOENS, Marnix, Karel, Christiane
Huntsman Ici Europe Ltd
Huntsman Polyurethanes
Intellectual Property Dept.
Everslaan 45
B-3078 Everberg
BELGIQUE

Date of mailing (day/month/year) 02 April 2001 (02.04.01)	
Applicant's or agent's file reference EUR 50725/WO	**IMPORTANT NOTIFICATION**
International application No. PCT/EP00/00039	**International filing date** (day/month/year) 05 January 2000 (05.01.00)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address	State of Nationality	State of Residence
HUNTSMAN ICI CHEMICALS, LLC 500 Huntsman Way Salt Lake City, UT 84108 United States of America	US	US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [X] the name [ ] the address [ ] the nationality [ ] the residence

Name and Address	State of Nationality	State of Residence
HUNTSMAN INTERNATIONAL LLC 500 Huntsman Way Salt Lake City, UT 84108 United States of America	US	US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[X] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer A. Karkachi Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 25 August 2000 (25.08.00)	
International application No. PCT/EP00/00039	**Applicant's or agent's file reference** EUR 50725/WO
International filing date (day/month/year) 05 January 2000 (05.01.00)	**Priority date** (day/month/year) 26 January 1999 (26.01.99)
Applicant LIMERKENS, Dominicus et al	

1. The designated Office is hereby notified of its election made:

   ☒ in the demand filed with the International Preliminary Examining Authority on:

   14 July 2000 (14.07.00)

   ☐ in a notice effecting later election filed with the International Bureau on:

   ____

2. The election ☒ was ☐ was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Charlotte ENGER Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
EUR 50725/WO		
International application No.	International filing date (*day/month/year*)	(Earliest) Priority Date (*day/month/year*)
PCT/EP 00/ 00039	05/01/2000	26/01/1999
Applicant		
HUNTSMAN ICI CHEMICALS, LLC et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readble form.

[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

[X] the text is approved as submitted by the applicant.

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

[X] the text is approved as submitted by the applicant.

[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ______

[ ] as suggested by the applicant.

[ ] because the applicant failed to suggest a figure.

[ ] because this figure better characterizes the invention.

[X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/00039

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/32 C08J9/06 //C08L75/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 692 516 A (BURGER HANS JOACHIM) 17 January 1996 (1996-01-17) claims	1-3,5,7, 8,22
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. , 31 October 1997 (1997-10-31) & JP 09 157427 A (MATSUMOTO YUSHI SEIYAKU CO LTD), 17 June 1997 (1997-06-17) abstract	4,6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 June 2000	06/07/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Oudot, R

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ıtional Application No
PCT/EP 00/00039

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0692516 A	17-01-1996	NONE	
JP 09157427 A	17-06-1997	NONE	

VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

PCT

INTERNATIONALER RECHERCHENBERICHT

(Artikel 18 sowie Regeln 43 und 44 PCT)

Aktenzeichen des Anmelders oder Anwalts	WEITERES VORGEHEN	siehe Mitteilung über die Übermittlung des internationalen Recherchenberichts (Formblatt PCT/ISA/220) sowie, soweit zutreffend, nachstehender Punkt 5
73 173		
Internationales Aktenzeichen	Internationales Anmeldedatum *(Tag/Monat/Jahr)*	(Frühestes) Prioritätsdatum *(Tag/Monat/Jahr)*
PCT/DE 00/ 00560	23/02/2000	27/04/1999
Anmelder		
MANNESMANN AG et al.		

Dieser internationale Recherchenbericht wurde von der Internationalen Recherchenbehörde erstellt und wird dem Anmelder gemäß Artikel 18 übermittelt. Eine Kopie wird dem Internationalen Büro übermittelt.

Dieser internationale Recherchenbericht umfaßt insgesamt 2 Blätter.

[X] Darüber hinaus liegt ihm jeweils eine Kopie der in diesem Bericht genannten Unterlagen zum Stand der Technik bei.

1. **Grundlage des Berichts**

   a. Hinsichtlich der **Sprache** ist die internationale Recherche auf der Grundlage der internationalen Anmeldung in der Sprache durchgeführt worden, in der sie eingereicht wurde, sofern unter diesem Punkt nichts anderes angegeben ist.

   [ ] Die internationale Recherche ist auf der Grundlage einer bei der Behörde eingereichten Übersetzung der internationalen Anmeldung (Regel 23.1 b)) durchgeführt worden.

   b. Hinsichtlich der in der internationalen Anmeldung offenbarten **Nucleotid- und/oder Aminosäuresequenz** ist die internationale Recherche auf der Grundlage des Sequenzprotokolls durchgeführt worden, das

   [ ] in der internationalen Anmeldung in Schriftlicher Form enthalten ist.

   [ ] zusammen mit der internationalen Anmeldung in computerlesbarer Form eingereicht worden ist.

   [ ] bei der Behörde nachträglich in schriftlicher Form eingereicht worden ist.

   [ ] bei der Behörde nachträglich in computerlesbarer Form eingereicht worden ist.

   [ ] Die Erklärung, daß das nachträglich eingereichte schriftliche Sequenzprotokoll nicht über den Offenbarungsgehalt der internationalen Anmeldung im Anmeldezeitpunkt hinausgeht, wurde vorgelegt.

   [ ] Die Erklärung, daß die in computerlesbarer Form erfaßten Informationen dem schriftlichen Sequenzprotokoll entsprechen, wurde vorgelegt.

2. [ ] **Bestimmte Ansprüche haben sich als nicht recherchierbar erwiesen** (siehe Feld I).

3. [ ] **Mangelnde Einheitlichkeit der Erfindung** (siehe Feld II).

4. Hinsichtlich der **Bezeichnung der Erfindung**

   [ ] wird der vom Anmelder eingereichte Wortlaut genehmigt.

   [X] wurde der Wortlaut von der Behörde wie folgt festgesetzt:

   NUTZUNG DES NIEDERSPANNUNGSNETZES INEINEM GEBAÜDE ZUM ÜBERTRAGEN UND ABSTRAHLEN VON HOCHFREQUENZMOBILFUNKSIGNALEN

5. Hinsichtlich der **Zusammenfassung**

   [X] wird der vom Anmelder eingereichte Wortlaut genehmigt.

   [ ] wurde der Wortlaut nach Regel 38.2b) in der in Feld III angegebenen Fassung von der Behörde festgesetzt. Der Anmelder kann der Behörde innerhalb eines Monats nach dem Datum der Absendung dieses internationalen Recherchenberichts eine Stellungnahme vorlegen.

6. Folgende Abbildung der **Zeichnungen** ist mit der Zusammenfassung zu veröffentlichen: Abb. Nr. 1

   [X] wie vom Anmelder vorgeschlagen

   [ ] keine der Abb.

   [ ] weil der Anmelder selbst keine Abbildung vorgeschlagen hat.

   [ ] weil diese Abbildung die Erfindung besser kennzeichnet.

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
P[illegible]E 00/00560

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 7 H04B3/54 H04B7/26

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 7 H04B H04M

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie°	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	GB 2 330 049 A (NORWEB PLC) 7. April 1999 (1999-04-07) Seite 19, Zeile 4 -Seite 22, Zeile 23 Seite 4, Zeile 19 -Seite 8, Zeile 16 ---	1-14
X	WO 99 00906 A (ADC TELECOMMUNICATIONS INC) 7. Januar 1999 (1999-01-07) Seite 1, Zeile 19 - Zeile 25 Seite 4, Zeile 27 -Seite 11, Zeile 16 -----	1-5, 10-14

☐ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

° Besondere Kategorien von angegebenen Veröffentlichungen :

"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

"E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist

"L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)

"O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht

"P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist

"T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist

"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden

"Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist

"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
29. Juni 2000	06/07/2000

Name und Postanschrift der Internationalen Recherchenbehörde	Bevollmächtigter Bediensteter
Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Larcinese, A

1

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
GB 2330049	A	07-04-1999	AU	1638999	A	29-04-1999
			AU	704011	B	01-04-1999
			AU	2262795	A	16-11-1995
			BG	100994	A	28-11-1997
			BR	9507402	A	07-10-1997
			CA	2188271	A	02-11-1995
			CZ	9603058	A	11-06-1997
			EP	0756786	A	05-02-1997
			EP	0913955	A	06-05-1999
			FI	964232	A	21-10-1996
			WO	9529537	A	02-11-1995
			GB	2302783	A,B	29-01-1997
			HU	76007	A	30-06-1997
			JP	9512394	T	09-12-1997
			NO	964432	A	04-12-1996
			NZ	284119	A	27-04-1998
			PL	316982	A	03-03-1997
WO 9900906	A	07-01-1999	AU	8168598	A	19-01-1999
			EP	0992125	A	12-04-2000

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D INTELLECTUAL PROPERTY ORGANIZATIO
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C08J 9/32, 9/06 // C08L 75/04

A1

(11) International Publication Number: WO 00/44821

(43) International Publication Date: 3 August 2000 (03.08.00)

(21) International Application Number: PCT/EP00/00039

(22) International Filing Date: 5 January 2000 (05.01.00)

(30) Priority Data:
99101359.0 26 January 1999 (26.01.99) EP

(71) Applicant *(for all designated States except US)*: HUNTSMAN ICI CHEMICALS, LLC [US/US]; 500 Huntsman Way, Salt Lake City, UT 84108 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: LIMERKENS, Dominicus [BE/BE]; Broekkantstraat 63, B-3680 Meeuwen-Gruitrode (BE). VAN DIJCK, Johan [BE/BE]; Boshovenstraat 23, B-3680 Meeuwen-gruitrode (BE). VAN EDOM, Bart [BE/BE]; Tiensevest 128/1, B-3000 Leuven (BE). WATSON, Rhona [GB/BE]; Onze Lieve Vrouwweg 3, B-3040 Huldenberg (BE).

(74) Agents: MOENS, Marnix, Karel, Christiane et al.; Huntsman Ici Europe Ltd, Huntsman Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: FOAMED THERMOPLASTIC POLYURETHANES

(57) Abstract

Process for the preparation of foamed thermoplastic polyurethanes characterised in that the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
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BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
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BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
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CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
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CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PATENT COOPERATION TREATY

CC 11/1

10 MEI 2001

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

MOENS, Marnix Karel Christiane
HUNTSMAN ICI (Europe) BVBA
Huntsman Polyurethanes
Intellectual Property Department
Everslaan 45
B-3078 Everberg
BELGIQUE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

	Date of mailing *(day/month/year)* 08.05.2001	
Applicant's or agent's file reference EUR 50725/WO	**IMPORTANT NOTIFICATION**	
International application No. PCT/EP00/00039	International filing date *(day/month/year)* 05/01/2000	Priority date *(day/month/year)* 26/01/1999
Applicant HUNTSMAN INTERNATIONAL LLC et al.		

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

   The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

   Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

   For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/ European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Aperribay, I Tel.+49 89 2399-8154

Form PCT/IPEA/416 (July 1992)

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PATENT COOPERATION TREATY

PCT

REC'D 10 MAY 2001

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference EUR 50725/WO	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP00/00039	International filing date *(day/month/year)* 05/01/2000	Priority date *(day/month/year)* 26/01/1999
International Patent Classification (IPC) or national classification and IPC C08J9/32		
Applicant HUNTSMAN INTERNATIONAL LLC et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report
   II ☐ Priority
   III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   IV ☐ Lack of unity of invention
   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   VI ☐ Certain documents cited
   VII ☐ Certain defects in the international application
   VIII ☒ Certain observations on the international application

Date of submission of the demand 14/07/2000	Date of completion of this report 08.05.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Radke, M Telephone No. +49 89 2399 8677

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/00039

I. Basis f the rep rt

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, pages:

1-16	as originally filed			

Claims, No.:

1-21	as received on	15/01/2001	with letter of	15/01/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-21
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-21
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-21
	No:	Claims	

2. Citations and explanations
   see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

R It m V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Cited literature

(a) Reference is made to the following documents:

D1: **EP-A-0 692 516**
D2: **WO-A-94/20 568**
D3: **WO-A-96/39 059**

(b) The documents **D2** and **D3** were not cited in the international search report; **D2** is mentioned on page 3 of the present application. Copies of **D2** and **D3** were appended to the written opinion.

(c) In the following arguments, page or column A, lines B to C will be cited as A/B-C.

2. Novelty

(a) Document **D1** discloses a foam made from
(1) a base polymer which may be TPU (see claim 3), and
(2) a non expanded foam concentrate based on polyvinylidene chloride, vinylidene fluoride or polyacrylonitrile yielding microspheres at an elevated temperature (see claim 5).

The subject-matter of the present claims differs from the disclosure in **D1** in that they require that the microspheres are filled with a hydrocarbon.

(b) Document **D2** describes TPU foams having densities in the range of from 130 to 300 g/l (see Table 3 on page 15, the column under the heading "Formteildichte").

The subject-matter of the present claims differs from the disclosure in **D2** in that they require the presence of microspheres.

(c) Document **D3** is directed to a golf shoe having a mid sole comprised of a foamed TPU/TPR blend, a foamed butadiene style rubber or a Hytrel/Surlyn blend which is preferably foamed with expanded resilient microspheres (see **D3**, 5/6-11). The only brand of expanded resilient microspheres mentioned in **D3** is Expancel 091 DE80 (see **D3**, 15/7). It is most likely that this type of microspheres is filled with an aliphatic or cyclic hydrocarbon as is Expancel 092 MB120 (which was employed in the examples of the present application).

The subject-matter of the present claims differs from the disclosure in **D3** in that **D3** only discloses external blowing agents and expanded microspheres as alternatives thus excluding the combination of both.

(d) For this reason the subject-matter of **claims 1 to 21** is novel.

3. Inventive step

(a) The problem to be solved by the present application was to provide low density TPUs having improved skin quality and which can be produced with reduced demould times (see 2/10-11 of the present application).

(b) The prior art cited above does not deal with the present problem. Table 2 on page 15 of the present application shows (see example 2 (comparative) vs. example 6) that the addition of the microspheres to the TPU containing a blowing agent reduces the demould times and improves the skin appearance.

(c) The subject-matter of **claims 1 to 21** is thus based on an inventive step.

Re Item VIII

Certain observations on the international application

1. The description is not adapted to the amended claims.

2. Example 4 should have been denoted as being comparative.

Amended set of claims

1. Process for the preparation of foamed thermoplastic polyurethanes characterised in that the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres and in the presence of an additional blowing agent, said microspheres containing a hydrocarbon.

2. Process according to claim 1 wherein the hydrocarbon is an aliphatic or cycloaliphatic hydrocarbon.

3. Process according to any of the preceding claims wherein an endothermic blowing agent is present.

4. Process according to any of the preceding claims wherein an exothermic blowing agent is present.

5. Process according to claim 3 or 4 wherein the endothermic blowing agent comprises bicarbonates or citrates.

6. Process according to any of claims 4-5 wherein the exothermic blowing agent comprises azodicarbonamide type compounds.

7. Process according to any of the preceding claims which is carried out by injection moulding.

8. Process according to any of the preceding claims which is carried out in a pressurized mould.

9. Process according to any of the preceding claims wherein the starting thermoplastic polyurethane is made by using a difunctional isocyanate composition comprising an aromatic difunctional isocyanate.

10. Process according to claim 9 wherein the aromatic difunctional isocyanate comprises diphenylmethane diisocyanate.

11. Process according to claim 10 wherein the diphenylmethane diisocyanate comprises at least 80% by weight of 4,4'-diphenylmethane diisocyanate.

12. Process according to claims 9-11 wherein the difunctional polyhydroxy compound comprises a polyoxyalkylene diol or polyester diol.

13. Process according to claim 12 wherein the polyoxyalkylene diol comprises oxyethylene groups.

14. Process according to claim 13 wherein the polyoxyalkylene diol is a poly(oxyethylene-oxypropylene) diol.

15. Process according to any of the preceding claims wherein the amount of microspheres is between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

16. Process according to claim 15 wherein the amount of microspheres is between 1.0 and 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

17. Process according to any of the preceding claims wherein the amount of blowing agent is between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

18. Process according to claim 17 wherein the amount of blowing agent is between 1.0 and 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

19. Foamed thermoplastic polyurethane obtainable by reacting a difunctional isocyanate composition with at least one difuctional polyhydroxy compound, in the presence of thermally expandable microspheres containing hydrocarbon, and in the presence of an additional blowing agent, said polyurethane having a density of not more than 700 kg/m^3 .

20. Foamed thermoplastic polyurethane according to claim 19 having a density of not more than 600 kg/m^3 .

21. Reaction system comprising TPU and thermally expandable microspheres containing a hydrocarbon, said reaction system comprising an additional blowing agent.

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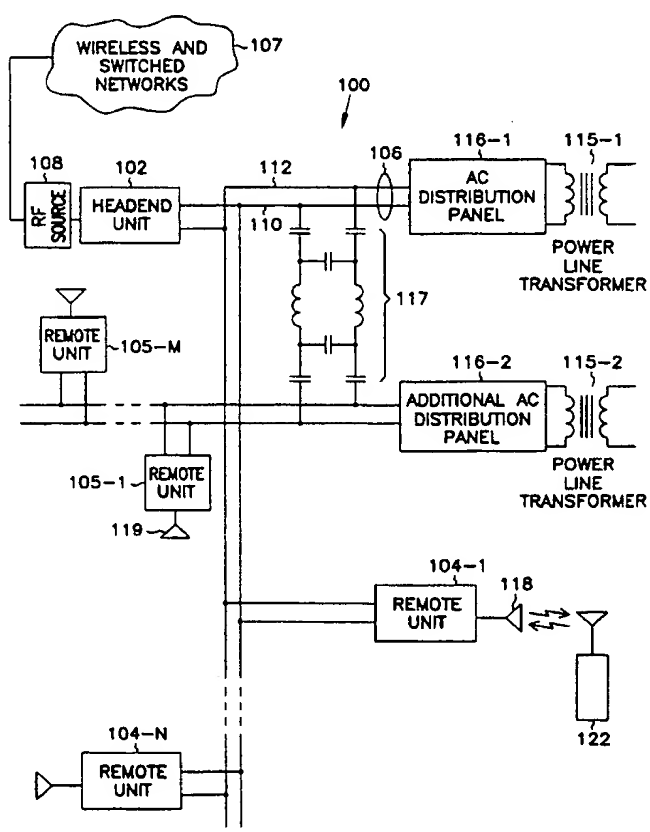
(57) Abstract

A system for distributing RF signals to users over power lines in a structure. The system includes a head end unit that receives RF signals in a first frequency range to be distributed to users in the structure. The head end unit is coupled to the power lines of the structure. RF signals are transmitted over the power lines in a second frequency range. The head end unit includes a frequency converter that translates RF signals between the first frequency range and the second frequency range. The system also includes a number of remote units. The remote units are coupled to the power lines and disposed throughout the structure to provide RF coverage within the structure. The remote units include frequency converters that convert signals between the first and second frequency ranges. Further, an antenna is coupled to each remote unit to transmit signals to and receive signals from the users in the first frequency range.



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SYSTEM AND METHOD FOR DISTRIBUTING RF SIGNALS

Technical Field of the Invention

The present invention relates generally to the field of communications and, in particular, to a system and method for distributing RF Signals over power lines within a substantially closed environment.

Background of the Invention

In recent years, the telecommunications industry has experienced rapid growth by offering a variety of new and improved services to customers. This growth has been particularly notable in the area of wireless communications, e.g., cellular and mobile radio systems. One of the factors that has led to the rapid growth in the wireless arena is the objective of allowing a user to be reached any time, and anywhere. Unfortunately, the industry has not been able to reach this goal even though large and small companies and various consortiums are frantically building vast networks in an effort to capture a share of this booming market.

Despite their efforts to provide seamless and blanket coverage for wireless telecommunications, some areas remain unaccessible. One particular difficulty is communication within a substantially closed environment, such as a building or other structure which can interfere with radio waves. The structure itself acts as a barrier and significantly attenuates or reduces the signal strength of the radio waves to the point that transmission is not possible at the frequency and power levels used in these systems.

The industry has toyed with a number of options to extend coverage into buildings and other substantially closed environments. For example, one solution to this problem has been to distribute antennas within the building. Typically, these antennas are connected to an RF signal source by dedicated coaxial cable, optical fiber, and, more recently, unshielded twisted pair wires. In such systems, various methods of signal conditioning and processing are used, ranging from straight bi-directional on-frequency amplification and band pass

filtering to select which service or service provider to transport, to frequency conversion methods to move the signals to a more desirable segment of the frequency spectrum for transport. Some systems also use passive antenna methods and "leaky" coaxial cable to radiate signals within the desired area without any signal conditioning. Unfortunately, the costs associated with installing such systems are prohibitively out of line with the benefits derived by the in-building coverage area provided by the system.

For the reasons stated above, and for other reasons stated below which will become apparent to those skilled in the art upon reading and understanding the present specification, there is a need in the art for an economically viable system and method for distributing RF signals in a substantially closed environment.

Summary of the Invention

The above mentioned problems with wireless communications systems and other problems are addressed by the present invention and will be understood by reading and studying the following specification. A system and method for distributing RF signals in a substantially closed environment are described which use the power lines in the closed environment to distribute signals to and from antennas within the closed environment.

In particular, an illustrative embodiment of the present invention includes a system for distributing RF signals to users over power lines in a structure. The system includes a head end unit that receives RF signals in a first frequency range to be distributed to users in the structure. The head end unit is coupled to the power lines of the structure. RF signals are transmitted over the power lines in a second frequency range. The head end unit includes a frequency converter that translates RF signals between the first frequency range and the second frequency range. The system also includes a number of remote units. The remote units are coupled to the power lines and disposed throughout the structure to provide RF coverage within the structure. The remote units include frequency converters that convert signals between the first and second frequency ranges.

Further, an antenna is coupled to each remote unit to transmit signals to and receive signals from the users in the first frequency range.

In another embodiment, a head end unit for an RF distribution system that transmits signals over AC power lines is provided. The head end unit includes a block converter that is coupled to receive signals from an RF source in a first frequency range. The block converter converts RF signals between the first frequency range and a second frequency range. The head end unit also includes a control processor that generates a control signal for remote units in the RF distribution system. Further, an ac power line interface is coupled to the block converter and the control processor for providing signals to and receiving signals from the ac power lines in the second frequency range.

In another embodiment, a remote unit for an RF distribution system that transmits signals over AC power lines is provided. The remote unit includes an antenna that communicates with wireless terminals using RF signals in a first frequency range. A block converter is coupled to the antenna and converts RF signals between the first frequency range and a second frequency range. A control processor receives a control signal from a head end unit and controls the operation of the remote unit. The remote unit also includes an ac power line interface coupled to the block converter and the control processor that provides signals to and receives signals from the ac power lines in the second frequency range.

In another embodiment, a method for transmitting RF signals in a substantially closed environment is provided. The method includes block converting RF signals between first and second frequency ranges at a head end unit. Further, the method calls for transmitting the RF signals in the second frequency range within the closed environment over ac power wiring between head end and remote units. The method also calls for block converting the RF signals between the first and second frequency ranges at the remote units. In this embodiment, the first frequency range is used for over-the-air transmission at both the head end and remote units.

Brief Description of the Drawings

Figure 1 is a block diagram of an embodiment of an RF distribution system constructed according to the teachings of the present invention;

Figure 2 is a block diagram of an embodiment of an head end unit for an RF distribution system according to the teachings of the present invention;

Figure 3 is a block diagram of an embodiment of a remote unit for an RF distribution system according to the teachings of the present invention;

Figure 4 is a schematic diagram of an embodiment of an AC power line interface for use in an RF distribution system according to the teachings of the present invention;

Figure 5 is a schematic diagram of another embodiment of an AC power line interface for use in an RF distribution system according to the teachings of the present invention; and

Figure 6 is a schematic diagram of another embodiment of an AC power line interface for use in an RF distribution system according to the teachings of the present invention.

Detailed Description of the Invention

In the following detailed description, reference is made to the accompanying drawings which form a part hereof, and in which are shown by way of illustration specific illustrative embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be utilized and that logical, mechanical and electrical changes may be made without departing from the spirit and scope of the present invention. The following detailed description is, therefore, not to be taken in a limiting sense.

In one embodiment, the present invention provides a radio frequency (RF) distribution system that transports RF signals throughout a building or other substantially closed environment to and from hand-held and desktop RF devices, e.g., cellular telephones, without the use of dedicated wiring or optical fiber. For purposes of this specification, the term "substantially closed

environment" or "closed structure" means an area in which the signal strength of a wireless communication system is diminished to a level so as to inhibit or reduce the effectiveness of communication by a wireless terminal with the wireless communication system. For example, a substantially closed environment includes, but is not limited to, a building, a campus of buildings, a mall or other similar type of structure. In this embodiment, the RF signals are impressed upon the existing AC power wiring of the substantially closed environment and extracted from it by using the techniques described below. RF signals that can be transported and distributed via these techniques include, but are not limited to, cellular, personal communication systems, land mobile, data, broadcast video, broadcast audio, paging, two-way and direct broadcast satellite, including low earth orbital satellites, wireless local area network (LAN) and wireless metropolitan area network (MAN) devices and RF telemetry.

The embodiments of the invention provide signal distribution using a unique method that does not require any new physical wiring or plant to be installed that is dedicated to the transport of the RF signals, but rather relies on using the existing AC power wiring, for example, as the physical interconnect medium. No other infrastructure other than head end and remote units is needed for operation. A number of difficulties are present when attempting to use the power lines as transmission lines, however.

In another area, some industries have developed methods for transmitting communication signals over power lines. For example, in the utility industry, many public utilities use "carrier current" methods of communications to, for example, read meters at a customer site from a central location. Typically, such carrier current methods of communication use low frequency (e.g., below 400 kilohertz) RF signals that are modulated with information related to the power companies' control and signaling needs. These modulated signals are transmitted over power lines between the power company and signaling and monitoring equipment located at its customer's location. Conventional practices indicate that only low frequencies are used in these systems because low frequency signals propagate better along the power grid than higher frequencies.

Thus, signaling over the power lines has received a very limited use outside the utility industry. Conventionally, AC power lines are understood to be an inherently inefficient transmission medium for radio frequency signals above 400-500 kilohertz.

Further, there are very large spectral noise components from 500 kilohertz up to approximately 50 megahertz that make this portion of the spectrum unusable for transmitting RF signals over power lines. Additionally, the presence of other ingress noise, e.g., shortwave broadcasters, in this portion of the spectrum make this portion of the spectrum virtually unusable as a transport frequency for power lines. It has been discovered, however, that RF frequencies in the range from approximately 100 megahertz to approximately 500 megahertz provide a good compromise between noise and attenuation for transmission on AC power lines. Above 500 megahertz, the RF signals attenuate too rapidly for the power lines to provide an acceptable transmission medium. Further, below 50 megahertz, too much noise on the power lines makes transmission unacceptable. However, in the range from 100 to 500 megahertz, RF power lines have been discovered to provide reasonable transport distances with reasonably low noise levels so as to allow transport over the power lines in this frequency range.

Figure 1 is a block diagram of an embodiment of an RF distribution system, indicated generally at 100, and constructed according to the teachings of the present invention. System 100 includes head end unit 102 that communicates with a number of remote units 104-1 through 104-N, and 105-1 through 105-M over power lines 106 in a closed structure, e.g., within a building, collection of buildings, or other substantially closed environment.

Head end unit 102 is coupled to RF source 108. RF source 108 may comprise, for example, a conventional antenna, an RF transport unit that uses either fiber-optics or copper cable to carry signals to and from a base station, or a co-located base station unit of a wireless communication system. RF source 108 is coupled to wireless and switched network 107 by either a wired or wireless communication path. Head end unit 102 is also connected to power lines 106,

including circuit ground 110 and circuit hot 112. In one embodiment, head end unit 102 includes a circuit that derives DC power for head end unit 102 from the AC power on power lines 106. Head end unit 102 also includes an AC power line interface circuit that is coupled to one of power lines 106 to allow RF signals to be passed between one of the power lines and head end unit 102. For example, the AC power line interface may be coupled to the circuit ground 110.

Power lines 106 are coupled to AC distribution panel 116-1 which receives power from transformer 115-1 as is conventional in wiring systems for a closed structure. Advantageously, power lines 106 may comprise, for example, a dedicated or closed wiring system. Such closed wiring systems include but are not limited to emergency lighting systems, exit sign system or other circuits that are dedicated to provide power to a specified and limited number of devices. These closed wiring systems provide the advantage of not being as susceptible to RF shorts when additional devices are plugged into the wiring system. Alternatively, lighting circuits in a building provide a relatively constant transmission system for communication between head end unit 102 and remote units 104-1 through 104-N, and 105-1 through 105-M.

In one embodiment, system 100 may be installed in a closed structure with power lines 106 that are divided into a number of isolated AC power circuits as shown in Figure 1. System 100 uses the power lines associated with ac distribution panel 116-1 and additional AC distribution panel 116-2 to distribute signals within the closed structure. When multiple AC power circuits are used in system 100, RF "jumpers" such as AC blocking/RF coupling circuit 117 are used to carry RF signals from one power circuit to another power circuit. AC blocking/RF coupling circuit 117 is tuned to a second frequency to facilitate RF coupling between the isolated AC power circuits.

Remote unit 104-1 is coupled to power lines 106. Namely, remote unit 104-1 includes a first terminal that is coupled to circuit hot line 112 and a second terminal that is coupled to circuit ground line 110. Remote unit 104-1 also is coupled to antenna 118 for distributing RF signals to and from wireless terminals 122 within the closed structure. Capacitor 120 is also coupled between remote

unit 104-1 and circuit ground 110. The remaining remote units are similarly coupled to power lines 106.

In operation, system 100 distributes RF signals to wireless terminals 122 using power lines 106 to route the signals to and from an antenna within the vicinity of wireless terminal 122. In the forward direction (to wireless terminal 122), RF source 108 receives signals for, e.g., wireless terminal 122 at an over-the-air frequency specified from wireless and switched networks 107. Head end unit 102 converts the over-the-air frequency from RF source 108 to an appropriate intermediate transport frequency for transmission over power lines 106. For example, it has been determined that the frequency range from approximately 100 megahertz to 500 megahertz provides reasonable transport distances with acceptable noise levels for power lines 106. Remote units 104-1 through 104-N, and 105-1 through 105-M convert the frequency range of the signals from power lines 106 to the over-the-air frequency range of the signals received from RF source 108. In this example, antenna 118 transmits the signals within the confines of the closed structure for receipt by wireless terminal 122.

In the reverse direction (from wireless terminal 122), wireless terminal 122 transmits signals to, e.g., remote unit 104-1. Remote unit 104-1 converts the over-the-air frequency of these signals to an intermediate transport frequency that is used on power lines 106. Head end unit 102 receives signals from remote units 104-1 through 104-N, and 105-1 through 105-M and converts the frequency range of the signals from power line 106 to the over-the-air frequency range. RF source 108 transmits these signals to wireless and switched networks 107. It is noted that AC blocking/RF coupling circuit 117 couples RF signals between the two AC power circuits to provide for communication between head end 102 and remote units 105-1 through 105-M.

Figure 2 is a block diagram of an embodiment of a head end unit, indicated generally at 200, for use in an RF distribution system according to the teachings of the present invention. Head end unit 200 is disposed in a convenient location in a substantially closed environment that is accessible to RF signal source 204 and has access to the AC power system in the building. Head

end unit 200 includes block converter 201 that converts RF signals between first and second frequency ranges. Block converter 201 includes duplexer/filter 202 that is coupled to RF source 204. Similarly, as with Figure 1, RF source 204 may comprise, for example, a conventional antenna, an RF transport unit that uses either fiber-optics or copper from a base station, or a co-located base station unit. Duplexer/filter 202 is coupled to both a forward and a reverse path. In the forward path, block converter 201 includes the serial connection of amplifier 206, mixer 208, amplifier 210, band pass filter 212, amplifier 214 and attenuator 216. Attenuator 216 in the forward path is coupled to triplexer/filter 218. In the reverse path, attenuator 220, amplifier 222, filter 224, amplifier 226, mixer 228 and amplifier 230 are coupled in series between triplexer/filter 218 and duplexer/filter 202.

Block converter 201 includes local oscillator 232. Local oscillator 232 is coupled to mixers 208 and 228. Additionally, local oscillator 232 receives a reference signal from reference oscillator 234.

Head end unit 200 also includes control processor/modem 236. Control processor/modem 236 receives the reference signal from reference oscillator 234. Control processor/modem 236 is also coupled to control attenuators 216 and 220 so as to establish an appropriate gain for the forward and reverse paths. Typically, this gain should be on the order of 20 to 40 dB. The amount of attenuation in attenuators 216 and 220 is established and stored in control processor/modem 236 when head end unit 200 is installed in a system. Control processor/modem 236 is also coupled to triplexer/filter 218 so as to provide a separate control signal to communicate with and control remote units in a system. The control signal is generated by head end unit 200 and exists outside any of the frequencies used for the transport of signals from RF source 204. This control signal contains set-up and alarm information for use by the remote units and initial and continuing calibration and event reporting that is used by the remote units. Control processor/modem 236 impresses the required information upon a control carrier and extracts responses from the remote units. The remote units, e.g., of the type shown and described with respect to Figure 3, also contain

a microprocessor and modem to communicate with the head end unit via the control signal, and act upon the information and report abnormal events back to the head end unit (alarms). The alarm and control information is available at head end unit 200 to be relayed back to the network operation center for a wireless system via a wireless modem or a modem on a wired telephone system.

Head end unit 200 also includes AC power line interface 238 that is coupled to an output of triplexer/filter 218. AC power line interface 238 provide for matching/isolating head end unit 200 to couple the RF energy into and extract RF energy from the AC power system. Head end unit 200 also includes AC to DC converter 238 that generates a DC power signal from the power on the AC line to provide power for head end unit 200. Other appropriate power sources can be used in place of the AC to DC converter.

In operation, head end unit 200 operates to convert RF signals between an over-the-air frequency range to a frequency range appropriate for distribution over AC power lines in the power distribution system. RF signals enter head end unit 200 from RF source 204 at duplexer/filter 202. Duplexer/filter 202 filters out signals outside the desired range of RF signals to be processed by head end unit 200. Amplifier 206 is a low-noise amplifier that amplifies the desired signals and passes them along to mixer 208. At mixer 208, the signals are heterodyned together with a signal from local oscillator 232, e.g., approximately 1500 Mhz for PCS, 1200 Mhz for cellular, or approximately 400 Mhz offset from the first frequency in the band, which is phase and frequency locked to reference oscillator 234 to provide end-to-end stability. The resulting signals from mixer 208 are in the intermediate frequency range from 100 to 500 megahertz. The signals are amplified and filtered by amplifiers 210 and filter 212, respectively. Amplifier 214 and attenuator 216 further adjust the amplification on the signals and provide the signals to triplexer/filter 218. AC power line interface 238 using, for example, a torodial inductive/capacitive network, provides proper isolation and maximum signal coupling conditions over a wide variety of loading conditions to pass the signals to the AC power system.

Control information is sent from head end unit 200 to the remote units by control processor/modem 236. Communications from control processor/modem 236 is accomplished by low-speed, 9600, frequency shift keyed (FSK) control signal that contains information generated by control processor/modem 236. This control information provides frequency stability information for the local oscillators of the remote units, control information for the on-off amplitude, auto-calibration adjustments required by the remote units, and alarm information for failure reporting.

In the reverse direction, AC power line interface 238 receives signals from the remote units over the AC power lines. Triplexer/filter 218 passes the signals through attenuator 220, amplifier 222, filter 224, amplifier 226 to mixer 228. At mixer 228, a signal from local oscillator 232 returns the signals to the over-the-air frequency range. Amplifier 230 amplifies the signals and provides the signals to duplexer/filter 202. Duplexer/filter 202 provides the signals from amplifier 230 to RF source 204 for transmission to an external wireless or wireless and switched network.

Figure 3 is a block diagram of an embodiment of a remote unit, indicated generally at 300, and constructed according to the teachings of the present invention. Remote unit 300 communicates signals to and from a wireless terminal over AC power lines to a head end unit such as head end unit 200 of Figure 2. Remote unit 300 includes antenna 302 that is used to transmit and receive signals to and from the wireless terminal. Antenna 302 is coupled to block converter 301. Block converter 301 includes duplexer/filter 304. Duplexer/filter 304 separates out signals into reverse and forward paths for remote unit 300. In the reverse path, block converter 301 includes amplifier 306, mixer 308, amplifier 310, filter 312, amplifier 314 and attenuator 316 that are coupled in series between duplexer/filter 304 and triplexer/filter 318. Similarly, in the forward path, block converter 301 includes attenuator 320, amplifier 322, filter 324, amplifier 326, mixer 328 and amplifier 330 coupled in series between triplexer/filter 318 and duplexer/filter 304. Remote unit 300 also includes control processor/modem 332 that is coupled to control attenuators 316 and 320

so as to adjust the gain in the forward and reverse paths when remote unit 300. Additionally, control processor/modem 332 is coupled to provide a control signal to and receive a control signal from triplexer/filter 318 of the type of signal described above with respect to head end unit 200 of Figure 2. Block converter 301 also includes local oscillator 334 that is coupled to mixers 308 and 328 to provide a reference frequency for use in mixing signals in the reverse and forward paths. Remote unit 300 also includes AC power line interface 336 that couples signals to and from triplexer/filter 318 with the AC power system. Remote unit 300 also includes an AC to DC converter 337 which generates a DC power signal for remote unit 300. Alternatively, other appropriate circuits can be used in place of AC to DC converter 337 to provide DC power for remote unit 300.

In operation, remote unit 300 translates signals between over-the-air frequencies and an intermediate frequency range used for transmission over the AC power lines. In the reverse direction, antenna 302 receives a signal from a wireless terminal in an over-the-air frequency range. This signal is passed to amplifier 306 by duplexer/filter 304. Mixer 308 converts, via heterodyne conversion, the frequency of the signals from amplifier 306 down to an intermediate frequency range for transmission over the AC power lines using the frequency of local oscillator 334. The translated signals are amplified in amplifier 310 and then filtered by band pass filter 312. Amplifier 314 and attenuator 316 are set so as to provide an appropriate overall gain for the reverse path. Triplexer/filter 318 passes the amplified and filtered signal from the reverse path to AC power line interface 336. AC power line interface 336 passes the signal to the AC power lines for transmission to a head end unit.

In the forward direction, AC power line interface 336 receives signals from the AC power lines and transmits these signals to triplexer/filter 318. Attenuator 320 and amplifier 322 are set so as to provide an appropriate gain, e.g. 40 dB, for the forward path. The output of amplifier 322 is filtered in band pass filter 324 and again amplified in amplifier 326. The forward signal is mixed by mixer 328 using the frequency of local oscillator 334 so as to translate

the frequency of the forward signal to the range for over-the-air communication. The signal from mixer 328 is amplified in amplifier 330 and provided to antenna 302 by duplexer/filter 304.

Antenna 302 may be integral with a body of remote unit 300. Antenna 302 alternatively could be a separate unit apart from remote unit 300 to facilitate placement of antenna 302. In one embodiment, antenna 302 of remote unit 300 is mounted within or on an exit sign in a building. Such exit signs are required in commercial buildings so that they are commonly visible to all the occupants of the facility and therefore provide a good antenna location.

In another embodiment, head end 102 of Figure 1 does not convert the frequency of the RF signals received from antenna 108. Rather, head end 102 leaves the RF signals at the over-the-air frequencies. In this manner, power lines 106 act as the antenna itself for broadcasting the RF signals within the building. This would eliminate the need for remote units 104 in certain situations, such as wood construction in private residences that use electrical wiring not installed in metallic conduits. This embodiment would result in a very cost-effective residential unit that could be easily deployed as an in-house booster, either as a one-way amplifier or using a bi-directional amplifier. Additionally, a carrier sense switching circuit could be attached to the return-path amplifier to have this amplifier turn on only when subscriber units are transmitting. This would prevent the low-level noise always generated by the return-path amplifier from occupying the channel and reducing the carrier-to-noise ratio of low-level desired signals that are on the frequency.

In another embodiment, the system of Figure 1 uses a dedicated feed from a base station. In this embodiment, an additional set of reverse path signals are used to simulate a diversity receive path. The additional set of reverse-path signals are heterodyned to another frequency in order to transport a diversity receive path back to the head end and present the signal set with its phase and amplitude components to the base station as the diversity receive path.

Figures 4, 5 and 6 illustrate various embodiments of AC power line interface circuits that can be used in, for example, head end unit 200 of Figure 2

or remote unit 300 of Figure 3. The various AC power line interface circuits are used to match head end unit 200 or remote unit 300 with the load of the AC power system. Additionally, an AC power line interface circuit also provides the function of isolating head end unit 200 or remote unit 300 from signal spikes on the AC power line.

In the embodiment shown in Figure 4, AC power line interface 400 includes a one-to-one transformer 402. A first input of transformer 402 is coupled to the AC power line. Additionally, a second input of transformer 402 is coupled through blocking capacitor 404 to the AC power line. Resistors 406 and 408 in this embodiment are provided primarily to aid in peak load protection for the head end unit 200 or remote unit 300. Additional blocking capacitors 410 and 412 are included in AC power line interface 400.

In an alternative embodiment shown in Figure 5, AC power line interface 500 includes a number of variable capacitors. Variable capacitors 502, 504, 506 and 508 comprise, for example, discrete capacitors that are switched in and out with a rotary switch. AC power line interface 500 also includes a fine-tuning capacitor 510 that is continuously variable. Finally, AC power line interface 500 also includes shunt inductance 512 that is switched in and out of AC power line interface 500 by switch 514. Shunt inductance 512, variable capacitors 502, 504, 506 and 508 and fine-tuning capacitor 510 are used to tune AC power line interface 500 to match the RF power line. The variable capacitors and shunt inductance are included to allow AC power line interface 500 to be adjusted on a case-by-case basis to improve signal transfer between the power lines and the head end or remote unit.

In another embodiment, AC power line interface 600 includes four-to-one transformer 602 that is coupled between the AC power line and either head end unit 200 or remote unit 300. AC power line interface circuit 600 also includes blocking capacitor 604 and protection diodes 606 and 608.

Conclusion

Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that any

arrangement which is calculated to achieve the same purpose may be substituted for the specific embodiment shown. This application is intended to cover any adaptations or variations of the present invention. For example, other matching/interface networks could be used in place of the embodiments shown in Figures 4, 5, and 6. Further, the number of amplifiers and placement of the amplifiers in the forward and reverse paths of the head end and remote units can be varies without departing from the spirit and scope of the present invention. Further, system 100 of Figure 1 can be used with an AC distribution system in a closed structure with a single AC distribution panel without the need for coupling circuit 117. System 100 can also be used in a closed structure with more than two AC distribution panels by using additional coupling circuits 117 to couple signals from one circuit to another. Thus, the system with two AC distribution panels shown in Figure 1 is shown by way of example, and not by way of limitation.

What is claimed is:

1. A system for distributing RF signals to users over power lines in a structure, the system comprising:

means for distributing RF signals from and to a number of remote units disposed throughout the structure to provide RF coverage; and

an antenna coupled to each remote unit to transmit signals to and receive signals from users.

2. A method for distributing RF signals to users over power lines in a structure, the system comprising:

distributing RF signals from and to a number of remote units disposed throughout the structure to provide RF coverage; and

using an antenna coupled to each remote unit to transmit signals to and receive signals from users.

3. The system of claim 1, and further including a base station coupled to the head end unit to provide the forward RF signals and to receive the reverse RF signals.

4. The system of claim 1, and further including an antenna coupled to the head end unit to provide the forward RF signals to the head end unit and to receive the reverse RF signals from the head end unit.

5. The system of claim 1, wherein the frequency converter includes a pair of mixers that are controlled by a common local oscillator.

6. The system of claim 1, wherein the frequency converter comprises a circuit that converts the first frequency range to a range between 100 and 500 Mhz.

7. The system of claim 1, wherein the head end unit and the remote units include variable amplifiers in a reverse path and a forward path.

8. The system of claim 1, wherein the antenna associated with a remote unit is disposed separate from the remote unit.

9. The system of claim 2, wherein each remote unit includes a modem for communicating with the control processor of the head end unit.

10. The system of claim 1, wherein the head end unit and the remote units are coupled to a controlled access AC power distribution system within the structure.

11. The system of claim 1, wherein the head end unit includes an AC power line interface that matches the head end unit with the load of the AC power lines.

12. A head end unit for an RF distribution system that transmits signals over AC power lines, the head end unit comprising:

a block converter that is coupled to receive signals from an RF source in a first frequency range, wherein the block converter converts RF signals between first and second frequency ranges;

a control processor that generates a control signal for remote units in the RF distribution system; and

an AC power line interface coupled to the block converter and the control processor that provides signals to and receives signals from the AC power lines in the second frequency range.

13. The head end unit of claim 12, wherein the block converter includes:

a mixer, an amplifier and a filter coupled in series between the RF source and the AC power line interface in a forward path;

a filter, an amplifier and a mixer coupled in series between the AC power line interface and the RF source in a reverse path;

a local oscillator coupled to the mixers; and

a reference oscillator coupled to provide a reference signal to the local oscillator and the control processor.

14. The head end unit of claim 12, wherein the AC power line interface includes a transformer coupled between the power lines and the block converter.

15. The head end unit of claim 12, wherein the AC power line interface includes a number of tunable capacitors coupled between the power lines and the block converter.

16. The head end unit of claim 12, wherein the control processor is further coupled to the forward and reverse paths so as to establish the gain of the forward and reverse paths.

17. A remote unit for an RF distribution system that transmits signals over AC power lines, the remote unit comprising:

an antenna that communicates with wireless terminals using RF signals in a first frequency range;

a block converter coupled to the antenna that converts RF signals between the first frequency range and a second frequency range;

a control processor that receives a control signal from a head end unit and controls the operation of the remote unit; and

an AC power line interface coupled to the block converter and the control processor for providing signals to and receiving signals from the AC power lines in the second frequency range.

18. The remote unit of claim 17, wherein the block converter includes:

a mixer, an amplifier and a filter coupled in series between the antenna and the AC power line interface in a reverse path;

a filter, an amplifier and a mixer coupled in series between the AC power line interface and the antenna in a forward path;

a local oscillator coupled to the mixers; and

a reference oscillator coupled to provide a reference signal to the local oscillator and the control processor.

19. The remote unit of claim 17, wherein the AC power line interface includes a transformer coupled between the power lines and the block converter.

20. The remote unit of claim 17, wherein the AC power line interface includes a number of tunable capacitors coupled between the power lines and the block converter.

21. The remote unit of claim 17, wherein the control processor is further coupled to the forward and reverse paths so as to establish the gain of the forward and reverse paths.

22. A method for transmitting RF signals in a substantially closed environment, comprising:

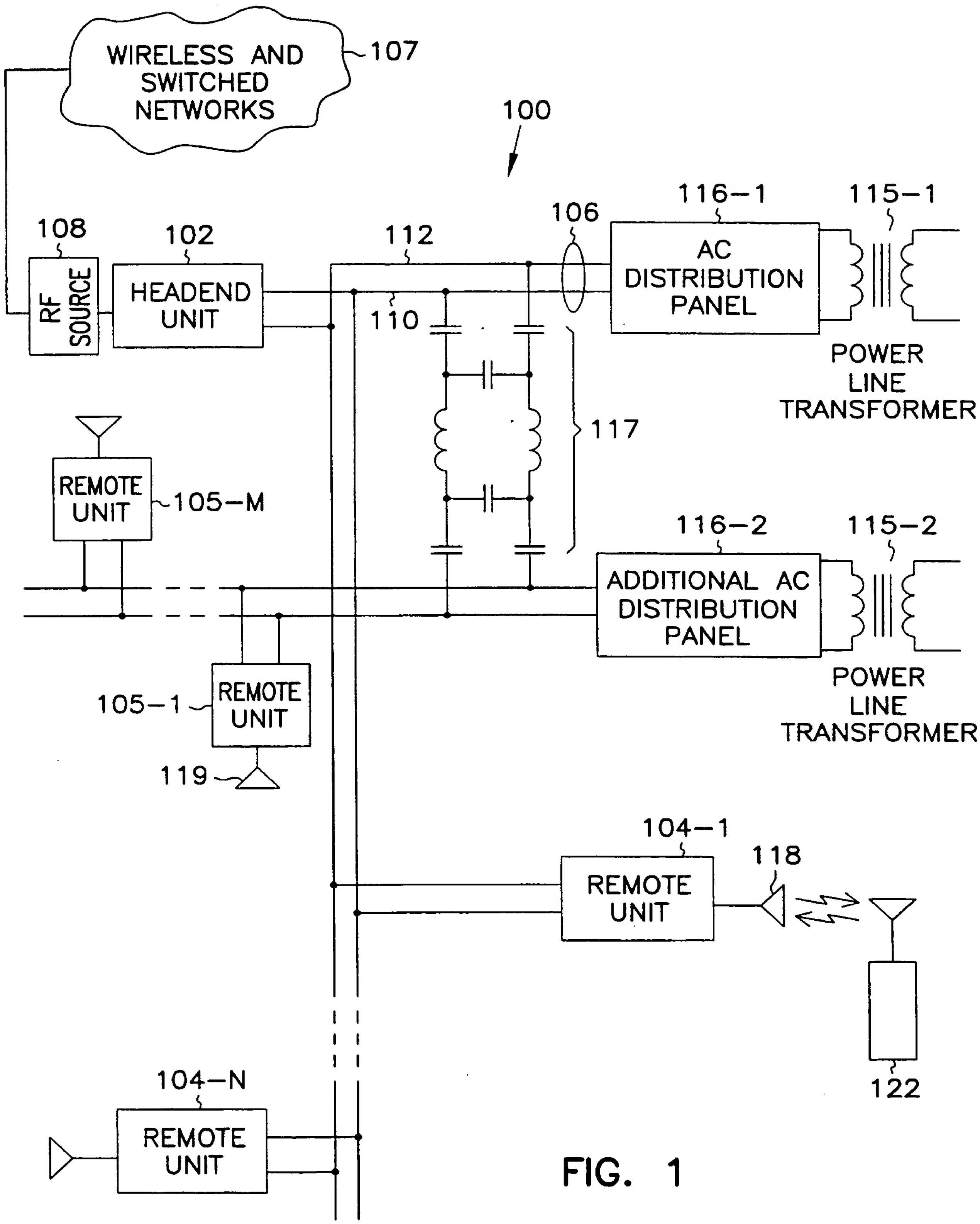
block converting RF signals between first and second frequency ranges at a head end unit;

transmitting the RF signals in the second frequency range within the substantially closed environment over AC power wiring between head end unit and remote units; and

block converting the RF signals between the first and second frequency ranges at the remote units, wherein the first frequency range is used for over-the-air transmission.

23. The method of claim 22, and further comprising the step of locking the frequency of a block converter at the remote units with a reference oscillator at the head end.

24. The method of claim 22, and further comprising the step of coupling RF signals between isolated power circuits within the substantially closed environment.


WIRELESS AND SWITCHED NETWORKS
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100
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RF SOURCE
102
HEADEND UNIT
112
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106
116-1
AC DISTRIBUTION PANEL
115-1
POWER LINE TRANSFORMER
117
REMOTE UNIT
105-M
116-2
ADDITIONAL AC DISTRIBUTION PANEL
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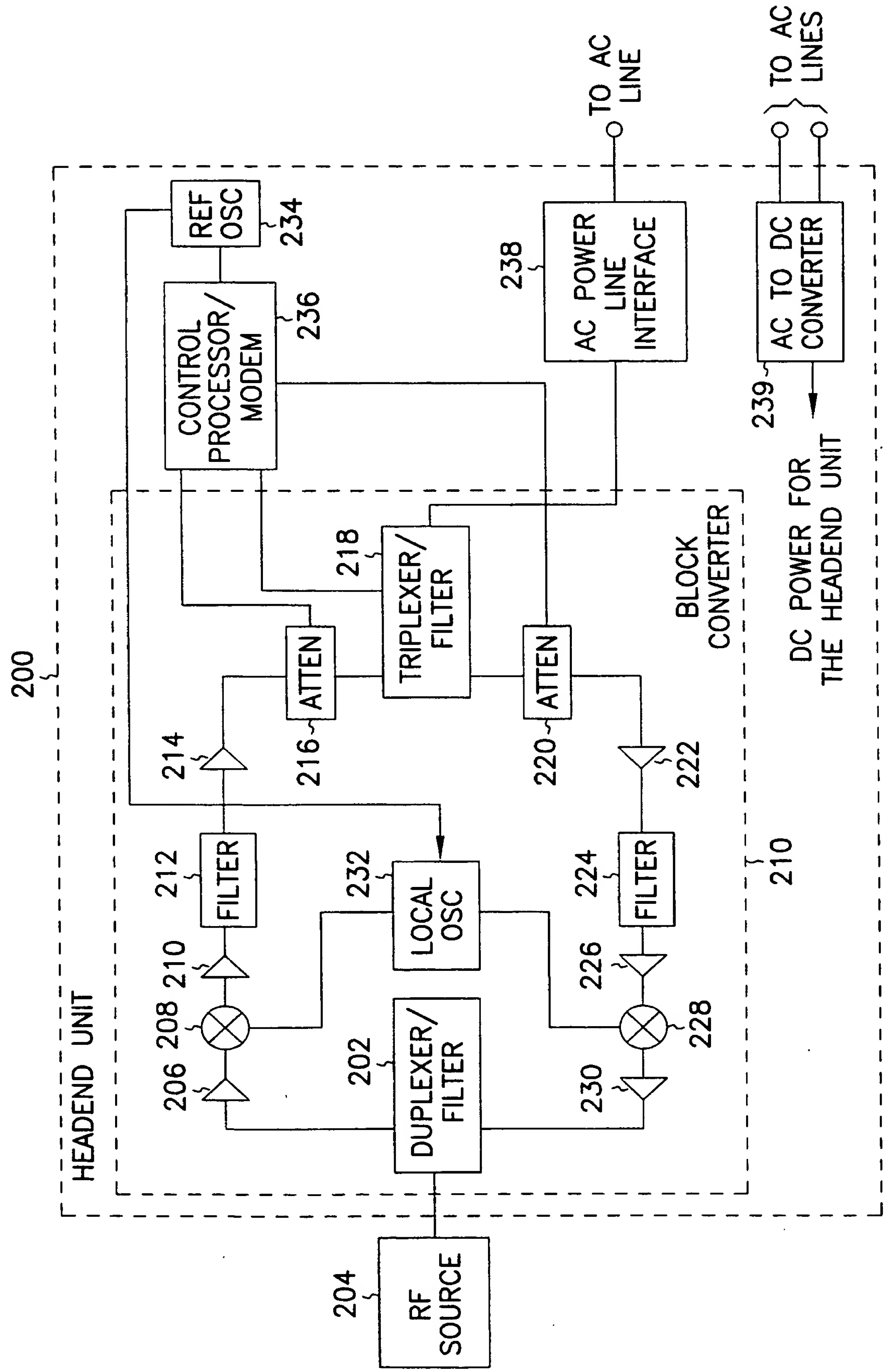
POWER LINE TRANSFORMER
105-1
REMOTE UNIT
119
104-1
REMOTE UNIT
118
122
104-N
REMOTE UNIT

FIG. 1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BLOCK CONVERTER
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RF SOURCE
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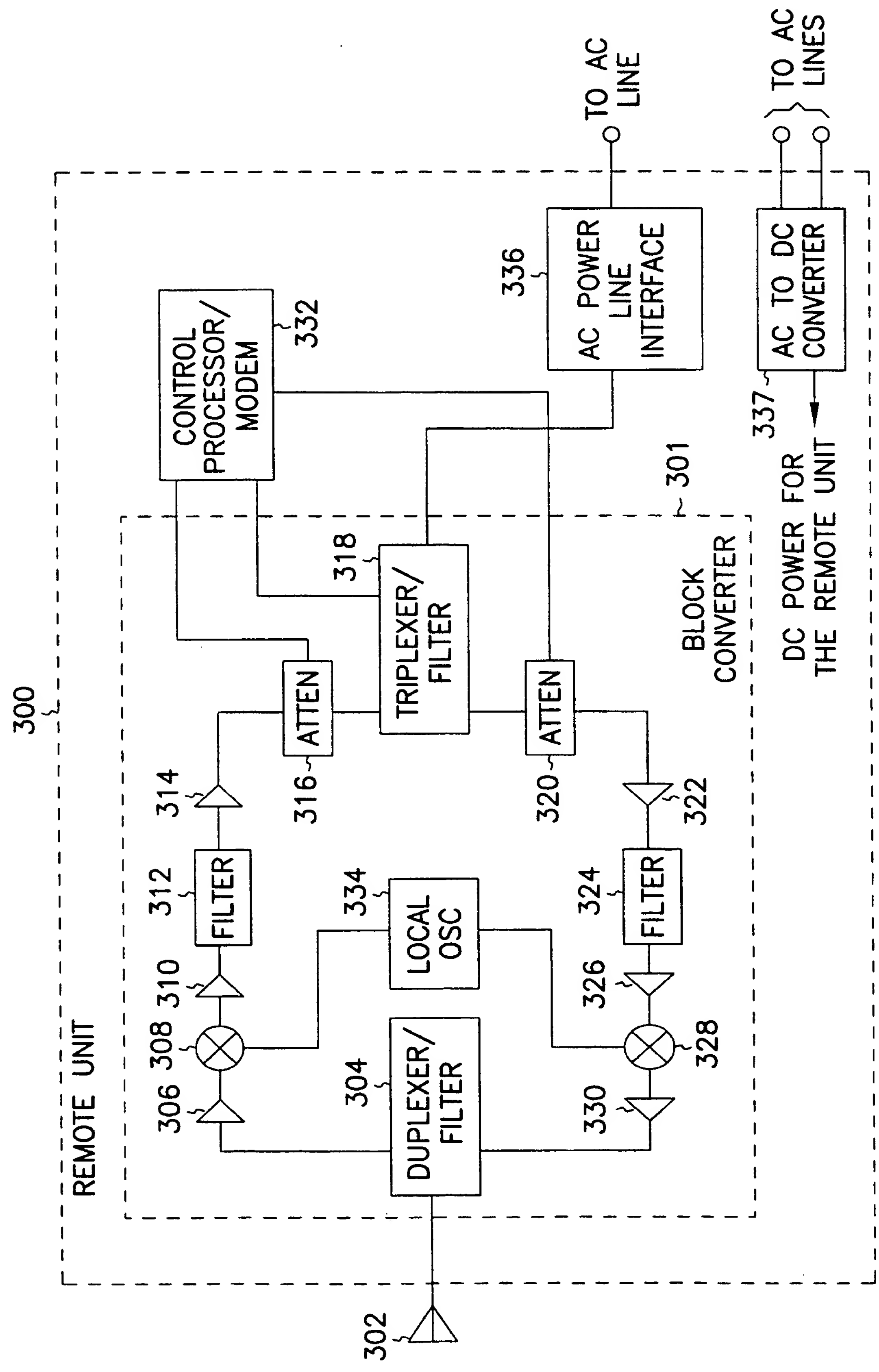
DUPLEXER/ FILTER
202
206
208
210
FILTER
212
214
ATTEN
216
TRIPLEXER/ FILTER
218
ATTEN
220
222
FILTER
224
226
228
230
LOCAL OSC
232
REF OSC
234
CONTROL PROCESSOR/ MODEM
236
AC POWER LINE INTERFACE
238
TO AC LINE
AC TO DC CONVERTER
239
TO AC LINES
DC POWER FOR THE HEADEND UNIT

FIG. 2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REMOTE UNIT
301
BLOCK CONVERTER
302
304
DUPLEXER/ FILTER
306
308
310
312
FILTER
314
316
ATTEN
318
TRIPLEXER/ FILTER
320
ATTEN
322
324
FILTER
326
328
330
334
LOCAL OSC
332
CONTROL PROCESSOR/ MODEM
336
AC POWER LINE INTERFACE
TO AC LINE
337
AC TO DC CONVERTER
TO AC LINES
DC POWER FOR THE REMOTE UNIT

FIG. 3

FIG. 4

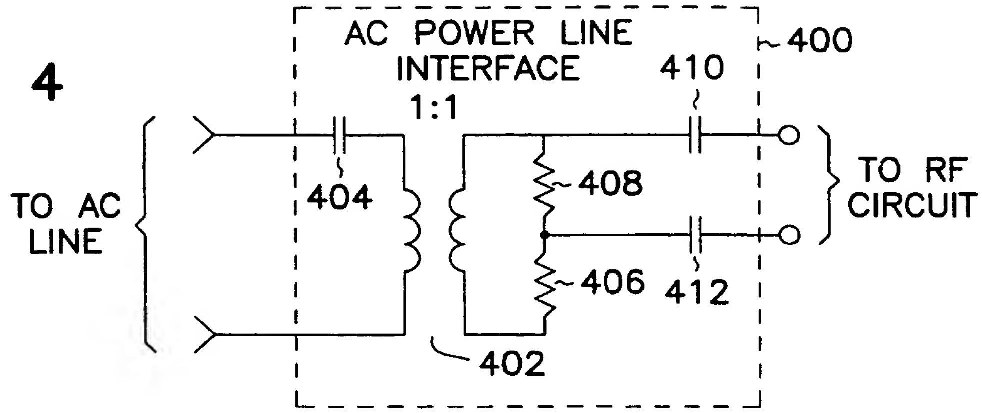


FIG. 5

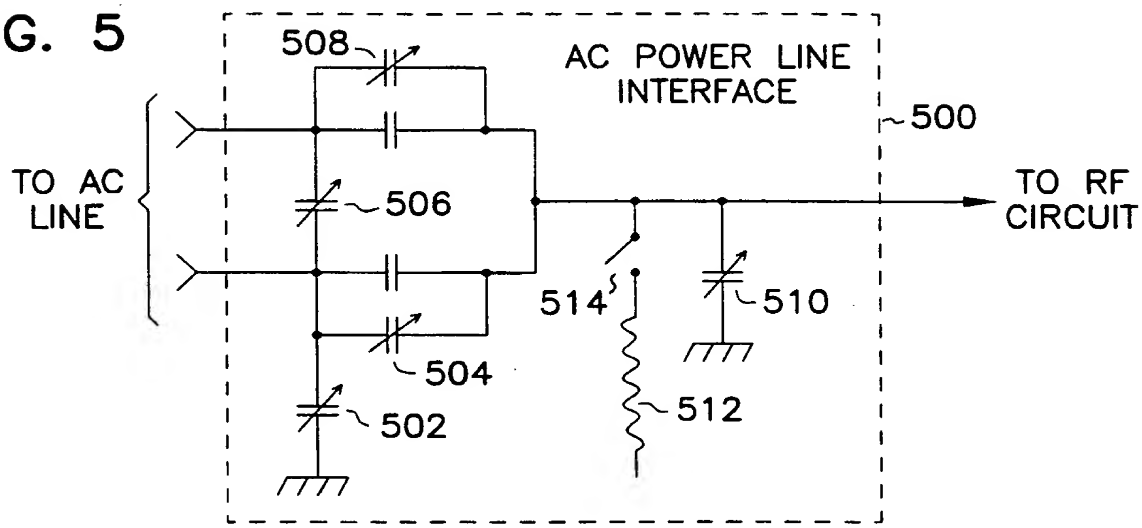
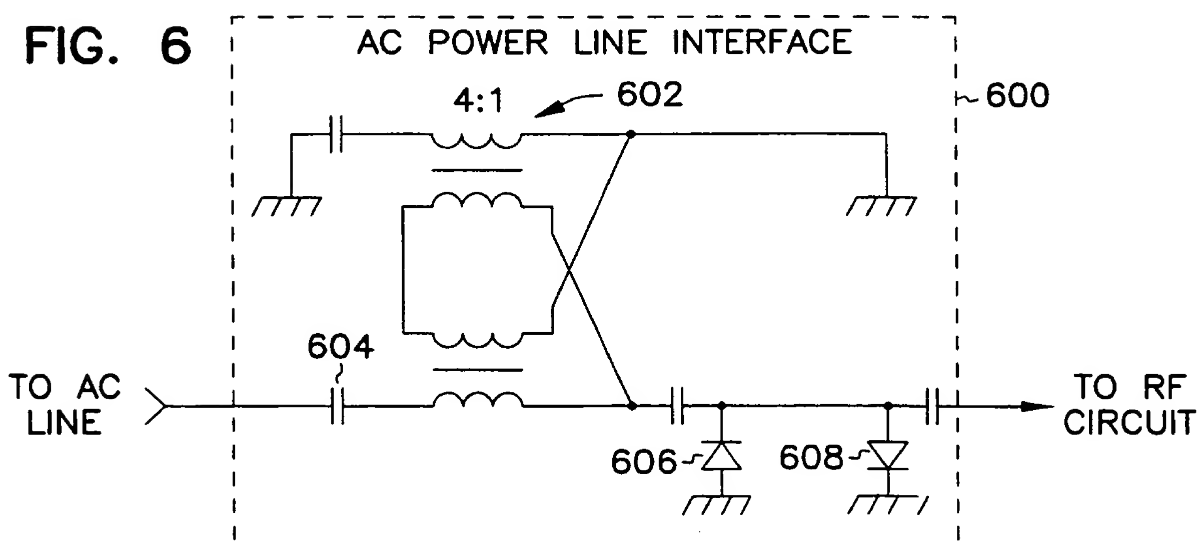


FIG. 6



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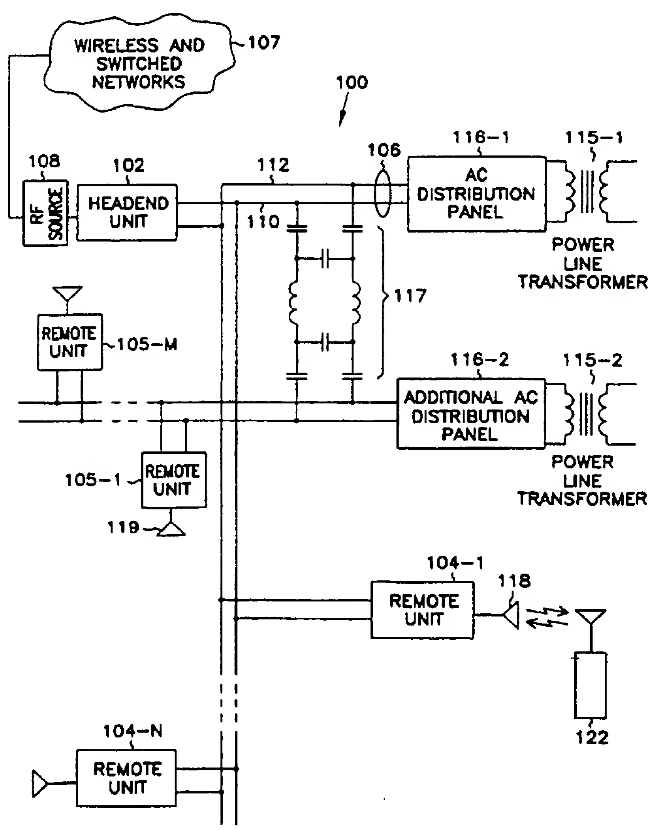
(57) Abstract

A system for distributing RF signals to users over power lines in a structure. The system includes a head end unit that receives RF signals in a first frequency range to be distributed to users in the structure. The head end unit is coupled to the power lines of the structure. RF signals are transmitted over the power lines in a second frequency range. The head end unit includes a frequency converter that translates RF signals between the first frequency range and the second frequency range. The system also includes a number of remote units. The remote units are coupled to the power lines and disposed throughout the structure to provide RF coverage within the structure. The remote units include frequency converters that convert signals between the first and second frequency ranges. Further, an antenna is coupled to each remote unit to transmit signals to and receive signals from the users in the first frequency range.



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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/13248

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 313 273 A (NORTHERN TELECOM LTD) 19 November 1997	1-3,6, 8-13, 16-18, 21-24
Y	see page 2, line 27 - page 3, line 7; figure 1 see page 8, line 30 - page 9, line 13 see page 13, line 32 - page 14, line 14; figure 3 see page 14, line 33 - page 15, line 7; figure 4 see page 15, line 24 - page 16, line 14 --- -/--	15,20

[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
17 February 1999	01/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De Iulis, M

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 29537 A (NORWEB PLC ;BROWN PAUL ANTHONY (GB)) 2 November 1995	1,2,4-8, 10,11, 22-24
Y	see page 19, line 4 - line 21; figure 1 see page 23, line 23 - page 24, line 9 see page 32, line 19 - page 33, line 3; figure 6 ---	15,20
X	US 5 319 634 A (BARTHOLOMEW DAVID B ET AL) 7 June 1994 see abstract; figure 4 -----	12,14, 17,19

2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/13248

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2313273 A	19-11-1997	AU 2904397 A	05-12-1997
		WO 9743836 A	20-11-1997
WO 9529537 A	02-11-1995	AU 2262795 A	16-11-1995
		BG 100994 A	28-11-1997
		BR 9507402 A	07-10-1997
		CA 2188271 A	02-11-1995
		CZ 9603058 A	11-06-1997
		EP 0756786 A	05-02-1997
		FI 964232 A	21-10-1996
		GB 2302783 A	29-01-1997
		HU 76007 A	30-06-1997
		JP 9512394 T	09-12-1997
		NO 964432 A	04-12-1996
		NZ 284119 A	27-04-1998
		PL 316982 A	03-03-1997
US 5319634 A	07-06-1994	AU 2861392 A	03-05-1993
		BR 9206605 A	28-03-1995
		CA 2119378 A	15-04-1993
		EP 0607304 A	27-07-1994
		JP 7501663 T	16-02-1995
		JP 2572940 B	16-01-1997
		WO 9307693 A	15-04-1993

Form PCT/ISA/210 (patent family annex) (July 1992)

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(54) Title: FOAMED THERMOPLASTIC POLYURETHANES

(57) Abstract

Process for the preparation of foamed thermoplastic polyurethanes characterised in that the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres.

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Foamed thermoplastic polyurethanes

Field of the invention

The present invention is concerned with a process for the preparation of foamed thermoplastic polyurethanes, novel foamed thermoplastic polyurethanes and reaction systems for preparing foamed thermoplastic polyurethanes.

Background of the invention

Thermoplastic polyurethanes, herein after referred to as TPUs, are well-known thermoplastic elastomers. In particular, they exhibit very high tensile and tear strength, high flexibility at low temperatures, extremely good abrasion and scratch resistance. They also have a high stability against oil, fats and many solvents, as well as stability against UV radiation and are being employed in a number of end use applications such as the automotive and the footwear industry.

As a result of the increased demand for lighter materials, a low density TPU needs to be developed which, in turn, represents a big technical challenge to provide, at minimum, equal physical properties to conventional low density PU.

It is already known to produce soles and other parts of polyurethane by a polyaddition reaction of liquid reactants resulting in an elastic solid moulded body. Up till now the reactants used were polyisocyanates and polyesters or polyethers containing OH-groups. Foaming was effected by adding a liquid of low boiling point or by means of CO_2, thereby obtaining a foam at least partially comprising open cells.

Reducing the weight of the materials by foaming the TPU has not given satisfactory results up to now. Attempts to foam TPU using well-known blowing agents as azodicarbonamides (exothermic) or sodiumhydrocarbonate (endothermic) based products were not successful for mouldings with reduced densities below 800 kg/m^3.

With endothermic blowing agents, a good surface finish can be obtained but the lowest density achievable is about 800 kg/m^3. Also, the processing is not very consistent and results in long demoulding times. Very little or no foaming is obtained at the mould surface due to a relatively low mould temperature, resulting in a compact, rather thick skin and a coarse cell core.

By using exothermic blowing agents, a lower density foam (down to 750 kg/m^3) with very fine cell structure can be achieved but the surface finish is not acceptable for most applications and demould time is even longer.

From the above it is clear that there is a continuous demand for low density TPUs having improved skin quality which can be produced with reduced demould times.

It has now been surprisingly found that foaming TPUs in the presence of thermally expandable microspheres, allows to meet the above objectives. Demould times are significantly reduced and the process can be carried out at lower temperatures, resulting in a better barrel stability. In addition, the use of microspheres even allows to further reduce the density while maintaining or improving the skin quality and demould time.

The present invention thus concerns a process for the preparation of foamed thermoplastic polyurethanes whereby the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres.

The low density thermoplastic polyurethanes thus obtained (density not more than 800 kg/m^3) have a fine cell structure, very good surface appearance, a relatively thin skin and show comparable physical properties to conventional PU which renders them suitable for a wide variety of applications.

The invention provides TPU products having outstanding low temperature dynamic flex properties and green strength at the time of demould, at density 800 kg/m^3 and below.

The term "green strength", as is known in the art, denotes the basic integrity and strength of the TPU at demould. The polymer skin of a moulded item, for example, a shoe sole and other moulded articles, should possess sufficient tensile strength and elongation and tear strength to survive a 90 to 180 degree bend without exhibiting surface cracks. The prior art processes often require 5 minutes minimum demould time to attain this characteristic.

In addition, the present invention therefore provides a significant improvement in minimum demould time. That is to say, a demould time of 2 to 3 minutes is achievable.

The use of microspheres in a polyurethane foam has been described in EP-A 29021 and US-A 5418257.

Adding blowing agents during the processing of TPUs is widely known, see e.g. WO-A 94/20568, which discloses the production of foamed TPUs, in particular expandable, particulate TPUs, EP-A 516024, which describes the production of foamed sheets from TPU by mixing with a blowing agent and heat-processing in an extruder, and DE-A 4015714, which concerns glass-fibre reinforced TPUs made by injection moulding TPU mixed with a blowing agent.

Nevertheless, none of the prior art documents discloses the use of thermally expandable microspheres to improve the skin quality of foamed low density TPU (density 800 kg/m^3 and even below) nor do these documents suggest the benefits associated with the present invention.

Detailed description

Thermoplastic polyurethanes are obtainable by reacting a difunctional isocyanate composition with at least one difunctional polyhydroxy compound and optionally a chain extender in such amounts that the isocyanate index is between 90 and 110, preferably between 95 and 105, and most preferably between 98 and 102.

The term 'difunctional' as used herein means that the average functionality of the isocyanate composition and the polyhydroxy compound is about 2.

The term "isocyanate index" as used herein is the ratio of isocyanate-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage. In other words, the isocyanate index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

It should be observed that the isocyanate index as used herein is considered from the point of view of the actual polymer forming process involving the isocyanate ingredient and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate-derivatives referred to in the art as quasi- or semi-prepolymers) or any active hydrogens reacted with isocyanate to produce modified polyols or polyamines, are not taken into account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens present at the actual elastomer forming stage are taken into account.

The difunctional isocyanate composition may comprise any aliphatic, cycloaliphatic or aromatic isocyanates. Preferred are isocyanate compositions comprising aromatic diisocyanates and more preferably diphenylmethane diisocyanates.

The polyisocyanate composition used in the process of the present invention may consist essentially of pure 4,4'-diphenylmethane diisocyanate or mixtures of that diisocyanate with one or more other organic polyisocyanates, especially other diphenylmethane diisocyanates, for example the 2,4'-isomer optionally in conjunction with the 2,2'-isomer. The polyisocyanate component may also be an MDI variant derived from a polyisocyanate composition containing at least 95% by weight of 4,4'-diphenylmethane diisocyanate. MDI variants are well known in the art and, for use in accordance with the invention, particularly include liquid products obtained by introducing carbodiimide groups into said polyisocyanate composition and/or by reacting with one or more polyols.

Preferred polyisocyanate compositions are those containing at least 80% by weight of 4,4'-diphenylmethane diisocyanate. More preferably, the 4,4'- diphenylmethane diisocyanate content is at least 90, and most preferably at least 95% by weight.

The difunctional polyhydroxy compound used has a molecular weight of between 500 and 20000 and may be selected from polyesteramides, polythioethers, polycarbonates, polyacetals, polyolefins, polysiloxanes, polybutadienes and, especially, polyesters and polyethers, or mixtures thereof. Other dihydroxy compounds such as hydroxyl-ended styrene block copolymers like SBS, SIS, SEBS or SIBS may be used as well.

Mixtures of two or more compounds of such or other functionalities and in such ratios that the average functionality of the total composition is about 2 may also be used as the difunctional polyhydroxy compound. For polyhydroxy compounds the actual functionality may e.g. be somewhat less than the average functionality of the initiator due to some terminal unsaturation. Therefore, small amounts of trifunctional polyhydroxy compounds may be present as well in order to achieve the desired average functionality of the composition.

Polyether diols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran in the presence, where necessary, of difunctional initiators. Suitable initiator compounds contain 2 active hydrogen atoms and include water, butanediol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,3-propane diol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-pentanediol and the like. Mixtures of initiators and/or cyclic oxides may be used.

Especially useful polyether diols include polyoxypropylene diols and poly(oxyethylene-oxypropylene) diols obtained by the simultaneous or sequential addition of ethylene or propylene oxides to difunctional initiators as fully described in the prior art. Random copolymers having oxyethylene contents of 10-80%, block copolymers having oxyethylene contents of up to 25% and random/block copolymers having oxyethylene contents of up to 50%, based on the total weight of oxyalkylene units, may be mentioned, in particular those

having at least part of the oxyethylene groups at the end of the polymer chain. Other useful polyether diols include polytetramethylene diols obtained by the polymerisation of tetrahydrofuran. Also suitable are polyether diols containing low unsaturation levels (i.e. less than 0.1 milliequivalents per gram diol).

Other diols which may be used comprise dispersions or solutions of addition or condensation polymers in diols of the types described above. Such modified diols, often referred to as 'polymer' diols have been fully described in the prior art and include products obtained by the in situ polymerisation of one or more vinyl monomers, for example styrene and acrylonitrile, in polymeric diols, for example polyether diols, or by the in situ reaction between a polyisocyanate and an amino- and/or hydroxyfunctional compound, such as triethanolamine, in a polymeric diol.

Polyoxyalkylene diols containing from 5 to 50% of dispersed polymer are useful as well. Particle sizes of the dispersed polymer of less than 50 microns are preferred.

Polyester diols which may be used include hydroxyl-terminated reaction products of dihydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 2-methylpropanediol, 3-methylpentane-1,5-diol, 1,6-hexanediol or cyclohexane dimethanol or mixtures of such dihydric alcohols, and dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof.

Polyesteramides may be obtained by the inclusion of aminoalcohols such as ethanolamine in polyesterification mixtures.

Polythioether diols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-alcohols or aminocarboxylic acids.

Polycarbonate diols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

Suitable polyolefin diols include hydroxy-terminated butadiene homo- and copolymers and suitable polysiloxane diols include polydimethylsiloxane diols.

Suitable difunctional chain extenders include aliphatic diols, such as ethylene glycl, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 2-methylpropanediol, 1,3-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, diethylene glycol, dipropylene glycol and tripropylene glycol, and aminoalcohols such as ethanolamine, N-methyldiethanolamine and the like. 1,4-butanediol is preferred.

The TPUs suitable for processing according to the invention can be produced in the so-called one-shot, semi-prepolymer or prepolymer method, by casting, extrusion or any other process known to the person skilled in the art and are generally supplied as granules or pellets.

Optionally, small amounts, i.e. up to 30, preferably 20 and most preferably 10, wt% based on the total of the blend, of other conventional thermoplastic elastomers such as PVC, EVA or TR may be blended with the TPU.

Any thermally expandable microspheres can be used in the present invention. However, microspheres containing hydrocarbons, in particular aliphatic or cycloaliphatic hydrocarbons, are preferred.

The term "hydrocarbon" as used herein is intended to include non-halogenated and partially or fully halogenated hydrocarbons.

Thermally expandable microspheres containing a (cyclo)aliphatic hydrocarbon, which are particularly preferred in the present invention, are commercially available. Such microspheres

are generally dry, unexpanded or partially unexpanded microspheres consisting of small spherical particles with an average diameter of typically 10 to 15 micron. The sphere is formed of a gas proof polymeric shell (consisting e.g. of acrylonitrile or PVDC), encapsulating a minute drop of a (cyclo)aliphatic hydrocarbon, e.g. liquid isobutane. When these microspheres are subjected to heat at an elevated temperature level (e.g. 150°C to 200°C) sufficient to soften the thermoplastic shell and to volatilize the (cyclo)aliphatic hydrocarbon encapsulated therein, the resultant gas expands the shell and increases the volume of the microspheres. When expanded, the microspheres have a diameter 3.5 to 4 times their original diameter as a consequence of which their expanded volume is about 50 to 60 times greater than their initial volume in the unexpanded state. An example of such microspheres are the EXPANCEL-DU microspheres which are marketed by AKZO Nobel Industries of Sweden ('EXPANCEL' is a trademark of AKZO Nobel Industries).

In a preferred embodiment, a blowing agent is added to the system, which may either be an exothermic or endothermic blowing agent, or a combination of both. Most preferably however, an endothermic blowing agent is added.

Any known blowing agent used in the preparation of foamed thermoplastics may be used in the present invention as blowing agents.

Examples of suitable chemical blowing agents include gaseous compounds such as nitrogen or carbon dioxide, gas (e.g. CO_2) forming compounds such as azodicarbonamides, carbonates, bicarbonates, citrates, nitrates, borohydrides, carbides such as alkaline earth and alkali metal carbonates and bicarbonates e.g. sodium bicarbonate and sodium carbonate, ammonium carbonate, diaminodiphenylsulphone, hydrazides, malonic acid, citric acid, sodium monocitrate, ureas, azodicarbonic methyl ester, diazabicylooctane and acid/carbonate mixtures. Preferrd endothermic blowing agents comprise bicarbonates or citrates.

Examples of suitable physical blowing agents include volatile liquids such as chlorofluorocarbons, partially halogenated hydrocarbons or non-halogenated hydrocarbons like propane, n-butane, isobutane, n-pentane, isopentane and/or neopentane.

Preferred endothermic blowing agents are the so-called 'HYDROCEROL' blowing agents as disclosed in a.o. EP-A 158212 and EP-A 211250, which are known as such and commercially available ('HYDROCEROL' is a trademark of Clariant).

Azodicarbonamide type blowing agents are preferred as exothermic blowing agents.

Microspheres are usually used in amount of from 0.1 to 5.0 parts by weight per 100 parts by weight of thermoplastic polyurethane. From 0.5 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane of microspheres are preferred. Most preferably, microspheres are added in amounts from 1.0 to 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

The total amount of blowing agent added is usually from 0.1 to 5.0 parts by weight per 100 parts by weight of thermoplastic polyurethane. Preferably, from 0.5 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane of blowing agent is added. Most preferably, blowing agent is added in amounts from 1.0 to 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

Additives which are conventionally used in thermoplastics processing may also be used in the process of the present invention. Such additives include catalysts, for example tertiary amines and tin compounds, surface-active agents and foam stabilisers, for example siloxane-oxyalkylene copolymers, flame retardants, antistatic agents, plasticizers, organic and inorganic fillers, pigments and internal mould release agents.

The foamed thermoplastic polyurethanes of the present invention can be made via a variety of processing techniques, such as extrusion, calendering, thermoforming, flow moulding or injection moulding. Injection moulding is however the preferred production method.

The presence of thermally expandable microspheres allows for a reduction in processing temperatures. Typically the process of the present invention is carried out at temperatures between 150 and 175°C.

Advantageously, the mould is pressurised, preferably with air, and the pressure is released during foaming. Although such process is known and commonly available from several machine producers, it has been surprisingly found that conducting the process of the present invention in a pressurised mould results in TPU articles having an excellent surface finish and physical properties, while having an even further reduced density (down to 350 kg/m^3).

Thermoplastic polyurethanes of any density between about 100 and 1200 kg/m^3 can be prepared by the method of this invention, but it is primarily of use for preparing foamed thermoplastic polyurethanes having densities of less than 800 kg/m^3, more preferably less than 700 kg/m^3 and most preferably less than 600 kg/m^3.

The thermoplastic polyurethane is customarily manufactured as pellets for later processing into the desired article. The term 'pellets' is understood and used herein to encompass various geometric forms, such as squares, trapezoids, cylinders, lenticular shapes, cylinders with diagonal faces, chunks, and substantially spherical shapes including a particle of powder or a larger-size sphere. While thermoplastic polyurethanes are often sold as pellets, the polyurethane could be in any shape or size suitable for use in the equipment used to form the final article.

According to another embodiment of the present invention, the thermoplastic polyurethane pellet of the present invention comprises a thermoplastic polyurethane body, the thermally expandable microspheres and a binding agent which binds the body and the microspheres. The binding agent comprises a polymeric component that has an onset temperature for its melt processing lower than the onset temperature of the melt processing range of the TPU. The pellets may also include blowing agents and/or additive components such as colorant or pigments.

The binding agent covers at least part of the thermoplastic polyurethane body. In a preferred embodiment, the thermoplastic polyurethane body and microspheres are substantially encapsulated by the binding agent. By 'substantially encapsulated' we mean that at least three-quarters of the surface of the thermoplastic polyurethane body is coated, and preferably at least about nine-tenths of the resin body is coated. It is particularly preferred for the binding agent to cover substantially all of the polyurethane body and microspheres. The amount of binding agent to the thermoplastic polyurethane may typically range from at least about 0.1% by weight and up to about 10% by weight, based on the weight of the thermoplastic polyurethane pellet. Preferably, the amount of the binding agent is at least about 0.5% by weight and up to 5% by weight, based on the weight of the thermoplastic polyurethane pellet.

Preferably, the binding agent has an onset temperature for its melt processing range that is below the onset temperature of the melt processing range of the thermoplastic polyurethane body. Thus the binding agent may be applied as a melt to the thermoplastic polyurethane body composition while the latter is a solid or substantially a solid. The onset temperature of the melt processing range ot the binding agent is preferably above about 20 degree C, and more preferably it is above 60 degree C, and even more preferably it is at least about 80 degree C. The onset temperature of the melt processing range of the polymeric component of the coating preferably has an onset temperature for its melt processing range at least about 20 degree C and even more preferably at least about 40 degree C. below, the onset temperature for the melt processing range of the thermoplastic polyurethane body. If the customized thermoplastic polyurethane pellets are to be dried using a dryer, then the melt processing range of the binding agent is preferably above the temperature of the dryer. In a preferred embodiment, the binding agent is chosen to prevent or slow water absorption so that a drying step before forming the desired article is unnecessary.

The binding agent may then be added to the TPU pellets by several different methods. In one method, the pellets are placed in a container with the coating composition while the pellets are still at a temperature above the onset temperature of the melt processing range of the binding agent. In this case the binding agent may be already melted or may be melted by the heat of the pellets or by heat applied externally to the container. For example, without limitation, the

binding agent may be introduced to the container as a powder when it is to be melted in the container. The binding agent can be any substance capable of binding the thermoplastic polyurethane body and the microspheres. Preferably the binding agent comprises a polymeric component. Examples of suitable polymeric components include polyisocyanates and/or prepolymers thereof.

The foamed thermoplastic polyurethanes obtainable via the process of the present invention are particularly suitable for use in any application of thermoplastic rubbers including, for example, footwear or integral skin applications like steering wheels.

Customized thermoplastic polyurethanes may be produced more efficiently using the process according to the present invention. The customized thermoplastic polyurethanes may be formed into any of the articles generally made with thermoplastic resins. Examples of articles are interior and exterior parts of automobiles, such as inside panels, bumpers, housing of electric devices such as television, personal computers, telephones, video cameras, watches, note-book personal computers; packaging materials; leisure goods; sporting goods and toys

In another embodiment, the present invention concerns a reaction system comprising (a) a TPU and (b) thermally expandable microspheres.

The invention is illustrated, but not limited, by the following examples in which all parts, percentages and ratios are by weight.

Examples

Example 1 (comparative)

TPU pellets (Avalon 62AEP; 'Avalon' is a trademark of Imperial Chemical Industries Ltd.) were dry blended with an endothermic blowing agent (1% NC175 powder or 2% INC7175ACR (which is a masterbatch equivalent); both supplied by Tramaco GmbH).

The dry blend was then processed on an injection moulding machine (Desma SPE 231) to form a test moulding of dimensions 19.5 *12.0 * 1 cm.

The processing temperatures for all the examples can be seen on Table 1. The physical properties obtained for all the examples can be seen on Table 2. Abrasion was measured according to DIN53516.

Example 2 (comparative)

The TPU of example 1 was dry blended with an exothermic blowing agent (Celogen AZNP130; available from Uniroyal) and was processed in the same way as in Example 1.
The minimum achievable density to avoid severe surface marking is 1000 kg/m^3 with an addition level of 0.3%.

Example 3 (comparative)

The TPU of example 1 was dry blended with a mixture of an exothermic and an endothermic blowing agent (0.3% Celogen AZNP130 and 0.7 % NC175) and processed in the same way as Example 1.

Example 4

The TPU of example 1 was dry blended with 4% of thermally expandable microspheres (Expancel 092 MB 120; commercially available from Akzo Nobel). This blend was processed in the same way as Example 1.

Example 5

The TPU of example 1 was dry blended with 2% of thermally expandable microspheres (Expancel 092 MB120) and an endothermic blowing agent (1% NC175 or 2% INC7175ACR) and processed in the same way as Example 1.

Example 6

The TPU of example 1 was dry blended with 2% of thermally expandable microspheres (Expancel 092 MB120) and 1% of an exothermic blowing agent (Celogen AZNP130). Again this was processed in the same way as Example 1.

Example 7

The TPU of example 1 was dry blended with 2% of thermally exandable microspheres (Expancel 092 MB120), 0.7 % of an endothermic blowing agent (NC175) and 0.3% of an exothermic blowing agent (Celogen AZNP130). Again this was processed in the same way as Example 1.

Example 8

The TPU of example 1 was dry blended with 2% of thermally expandable microspheres (Expancel 092 MB120) and an endothermic blowing agent (1% NC175 or 2% INC7175ACR). This was processed on a Main Group injection moulding machine.

Example 9

The TPU of example 1 was dry blended with 2.0% of thermally expandable microspheres (Expancel 092 MB120) and 2% of an exothermic blowing agent (IM7200; commercially available from Tramaco GmbH). This dry blend was processed on a Main Group machine with an air injection system (Simplex S16).

Example 10

The TPU of example 1 was dry blended with 2.5% of thermally expandable microspheres (EXP 092 MB120) and 2% of an exothermic blowing agent (IM7200). This dry blend was processed on a Main Group machine with an air injection system (Simplex S16).

Table 1 : Processing Temperatures of Injection Moulding

	Zone 1	Zone 2	Zone 3	Nozzle	Mould Temp.(C)
Ex.1*	180	185	190	185	50
Ex.2*	175	180	185	180	50
Ex.3*	180	185	190	185	50
Ex.4	155	160	165	160	50
Ex.5	160	165	170	165	50
Ex.6	160	165	170	165	50
Ex.7	160	165	170	165	50
Ex.8	155	160	165	160	40
Ex.9	155	160	165	160	25
Ex.10	155	160	165	160	25

* : comparative example

Table 2 : Properties

	Density (kg/m^3)	Hardness (Shore A)	Abrasion (mg)	Flex. Resistance (No. of cycles)	Demould time (seconds)	Skin Appearance
Ex.1*	810	61	53	>100.000	180	Excellent
Ex.2*	750	61	70	>100.000	210	Bad
Ex.3*	800	61	60	>100.000	180	Good
Ex.4	800	68	120	>100.000	120	Excellent
Ex.5	700	58	105	>100.000	130	Excellent
Ex.6	670	57	130	>100.000	150	Good
Ex.7	700	58	110	>100.000	130	Excellent
Ex.8	550	51	125	>100.000	180	Excellent
Ex.9	450	46	105	>100.000	180	Excellent
Ex.10	350	40	125	>100.000	180	Excellent

* : comparative example

Example 11

Example 11 provides for TPU pellets comprising microspheres formulated with binding agent. TPU pellets were pre-heated in a hot air oven at 100°C. Then as a binding agent, an isocyanate prepolymer based on Daltorez® P321 and Suprasec® MPR is prepared at 80°C. The binding agent (1-2% by weight) is then mixed into the TPU pellets to fully wet the surface of the TPU. The additives are then added and mixing continues until a homogeneous distribution of the additives on the surface of the TPU pellets is achieved. This mixture is then discharged into a polythene container and cooled to 10°C to allow the coating to solidify. This 'cake' is then de-agglomerated by hand and is ready for use in the injection molding machine.

These coated pellets were processed on the injection molding machine and sucessfully blown to densities of 0.73 g/cc.
Daltorez ®P321 is a polyester based polyol based on adipic acid and 1,6 hexanediol
Suprasec® MPR is pure MDI

Claims

1. Process for the preparation of foamed thermoplastic polyurethanes characterised in that the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres.

2. Process according to claim 1 wherein the thermally expandable microspheres contain a hydrocarbon.

3. Process according to claim 2 wherein the hydrocarbon is an aliphatic or cycloaliphatic hydrocarbon.

4. Process according to any of the preceding claims wherein an endothermic blowing agent is present.

5. Process according to any of the preceding claims wherein an exothermic blowing agent is present.

6. Process according to claim 4 or 5 wherein the endothermic blowing agent comprises bicarbonates or citrates.

7. Process according to any of claims 4-6 wherein the exothermic blowing agent comprises azodicarbonamide type compounds.

8. Process according to any of the preceding claims which is carried out by injection moulding.

9. Process according to any of the preceding claims which is carried out in a mould pressurized with air.

10. Process according to any of the preceding claims wherein the starting thermoplastic polyurethane is made by using a difunctional isocyanate composition comprising an aromatic difunctional isocyanate.

11. Process according to claim 10 wherein the aromatic difunctional isocyanate comprises diphenylmethane diisocyanate.

12. Process according to claim 11 wherein the diphenylmethane diisocyanate comprises at least 80% by weight of 4,4'-diphenylmethane diisocyanate.

13. Process according to any of the preceding claims wherein the difunctional polyhydroxy compound comprises a polyoxyalkylene diol or polyester diol.

14. Process according to claim 13 wherein the polyoxyalkylene diol comprises oxyethylene groups.

15. Process according to claim 14 wherein the polyoxyalkylene diol is a poly(oxyethylene-oxypropylene) diol.

16. Process according to any of the preceding claims wherein the amount of microspheres is between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

17. Process according to claim 16 wherein the amount of microspheres is between 1.0 and 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

18. .Process according to any of claims 4-17 wherein the amount of blowing agent is between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

19. Process according to claim 18 wherein the amount of blowing agent is between 1.0 and 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

20. Foamed thermoplastic polyurethane having a density of not more than 700 kg/m^3.

21. Foamed thermoplastic polyurethane having a density of not more than 600 kg/m^3 .

22. Reaction system comprising :

TPU

thermally expandable microspheres.